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A CERAMIC PIGMENT BASED ON A BY-PRODUCT OF NICKEL PRODUCTION

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A ceramic pigment that is a by-product of autoclave production of nickel is studied. Good technological properties and economic effectiveness of glazes containing this pigment are demonstrated. High-quality colored glaze coatings are obtained on porcelain and faience articles. The experimental results are confirmed by industrial tests.

Production of ceramic pigments and colorants for glasses and vitreous coatings involves substantial consumption of energy, which results from the need to obtain a high-purity end product with a large specific surface. Therefore, research on production of nontraditional ceramic pigments (colorants) based on recycled waste and by-products generated by various sectors of industry has great practical significance [1].

An analysis of the properties of slags, by-products, and waste of nonferrous metallurgy indicates that autoclave waste of nickel production possesses physical and chemico-mineralogical properties that are similar to the properties of iron oxide pigment used in production of porcelain and faience products.

Autoclave waste of nickel production is a finely disperse red powder (particle size 3 – 5 μm). The size of the particles of traditional iron oxide pigment is larger approximately an order of magnitude. Its composition is as follows (wt.%): up to 70 iron oxides, up to 7 silicon dioxide, up to 5 aluminum oxide, up to 4 alkali-earth metal oxides, and up to 1 alkali metals. As distinct from traditional brown pigment, the waste also contains up to 5% sulfur compounds, and its calcination loss reaches 10%.

The methods of optical microscopy and x-ray phase and differential thermal analysis established that the autoclave waste is represented mostly by hematite (75 – 80%), iron sulfate (10 – 15%), and iron sulfide (5 – 10%).

Preliminary calcination of the waste at different temperatures led to a change in its color and aggregation of its particles. The powder acquired a dark brown color. Individual grains reached a size of 0.1 mm. These changes in the powder are most likely caused by the exothermic reaction of iron sulfide oxidation. Therefore, the waste was tested without preliminary calcination.

In the course of heating the autoclave waste directly contained in the glaze coating, simultaneous reactions of disassociation and oxidation take place that result in formation of sulfur oxides and iron oxides:

$$5Fe_2(SO_4)_3 + 6FeS_2 + 15O_2 =$$
$$3FeO + 2Fe_2O_3 + 3Fe_2O_3 + 12SO_2\uparrow + 15SO_3\uparrow.$$

These reactions were investigated using the methods of the thermodynamics of silicates [2]. The reactions are almost fully completed in the temperature interval of 600 – 700°C, and their equilibrium constants are equal to 10^{10} – 10^{12}. Consequently, the reaction products contain the reactants (iron sulfate and sulfide) in the amount of thousandths of a percent, i.e., at the level of micro-impurities. Therefore, a negative effect of the reactants in the residual concentrations is insignificant or nonexistent. Furthermore, the chemical reactions presented are completed before the start of glaze-coating formation, so the latter does not impede the course of these reactions. Therefore, there should be no gas bubbles or pinholes caused by the nontraditional pigment.

Autoclave waste from nickel production at the Norilsk Mining and Metallurgical Works was tested under laboratory and industrial conditions as a ceramic pigment in preparing fritted zirconium glazes for porcelain and faience mixtures, using various methods for pigment introduction:

– in the dry state together with the glaze components in milling;

– in the form of a suspension added to the glaze slip with subsequent mixing in a high-speed ball mill for 0.5 h.

The amount of introduced pigment varied from 2 to 8% dry weight. The glaze obtained was filtered before its deposition on the article, and its residue on a No. 008 sieve was 0.08 – 0.09%.

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The tinted glaze had stable parameters of density (1.52 – 1.54 g/cm^3) and fluidity (first flow 8 – 9 sec, second flow 14 – 16 sec) that coincided with the same parameters in glazes with traditional pigments.

Different methods of glaze application were tested: spraying, casting, and immersion. The glaze was deposited by spraying on faience facade tiles with double firing, by casting on faience tiles with one-time firing, and by immersion on porcelain articles. The drying and firing of ceramic articles using the new ceramic pigment were carried out according to the standard procedures.

All methods of preparation and deposition of glaze showed positive results. The coatings had a mirror-like luster and homogeneous monotonic tinting. Depending on the amount of introduced pigment, the color varied from light brown (2%), brown (4%), and dark brown (6%) to dark brown with a cherry shade (8%). The glaze coatings are resistant in a 3% hydrochloric acid solution (7.6 mg/cm^2) and have good alkali resistance in a 4% soda solution. Their thermal resistance is 170 – 190°C, and crazing is absent.

Comparative testing of samples containing traditional iron oxide pigment indicated that compared to the traditional pigment, a 2.0 – 2.5% smaller amount of autoclave waste is required to produce a brown coating of equal quality.

The tests established good technological properties of glazes containing the autoclave waste as the colorant. The new colorant does not modify the glaze slip properties, makes it possible to shorten the time of glaze preparation, and provides a good quality of the coating. The economic effect of pigment based on autoclave waste of nickel production consists not only in the difference in the material prices but also in lower energy consumption in glaze preparation.

The use of a production of nickel by-product makes it possible to expand the range of pigments and to reduce the cost of production of tinted vitreous coatings. At the same time, the recycling of waste of nonferrous metallurgy will have a positive effect on the technical and economic parameters of this industry and will contribute to improvement of the ambient environment.

REFERENCES

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